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# Organoplatinum(II) complexes containing disubstituted dithioxamides: evidence for an S,S′ Pt coordinated neutral dithioxamide acting as an anion binding agent

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**Abstract**

*cis*-[$PtL_2R_2$] (L = $Me_2SO$ or $Me_2S$; R = Me or Ph) species react with N,N′-disubstituted dithioxamides $H_2$-$R'_2$-DTO (R′ = methyl, benzyl, n-butyl) leading to a new class of organoplatinum compounds of general formula [PtL(R)(H-$R'_2$-DTO)] (**1**). These are the first reported organometallic complexes containing an S,S′ Pt chelated rubeanate. The new compounds react with some neutral ligands L′ (L′ = carbon monoxide, phosphines and thioureas) giving [PtL′(R)(H-$R'_2$-DTO)] (**2**) products, which are totally unreactive toward nitrogen bases such as amines, pyridines and anilines. The compound *trans*-[Pt($Me_2SO$)$_2$MeCl] reacts with $H_2$-$bz_2$-DTO forming the contact ion pair {Pt($Me_2SO$)Me($H_2$-$bz_2$-DTO)$^+$,($Cl^-$)} (**3**); this is a non-isolable species since the Pt–$CH_3$ bond is cleaved by acidic hydrogens of the coordinated neutral dithioxamide leading to the formation of methane and [Pt($Me_2SO$)Cl(H-$bz_2$-DTO)] (**4**). A structure for the tight ion pair {Pt($Me_2SO$)Me($H_2$-$bz_2$-DTO)$^+$,($Cl^-$)} is proposed in which the coordinated neutral dithioxamide acts as an anion binding agent.

*Keywords:* Platinum complexes; Dialkyl complexes; Dithioxamide complexes

## 1. Introduction

At the end of the fifties, Chatt and Shaw reported the first complexes in which monodentate groups were bound to platinum(II) by a single metal(II)–carbon σ bond [1]. These compounds also contained phosphines and arsines, which for some time were believed to be the only ligands capable of stabilising the platinum(II)–carbon σ bond. The great stability of organoplatinum phosphine and arsine compounds is unquestionable; notwithstanding, complexes with organic ligands bound monofunctionally to platinum(II) that are stabilised by other ligands such as diolefines, pyridine, 2,2′-bipyridyl, 1,10-phenanthroline and so on, were prepared afterwards in great numbers [2].

More recently, σ-bonded organoplatinum(II) species have been synthesised in which the neutral ligands were dialkylsulfides [3] or dimethyl sulfoxide [4]. The sulfide complexes were generally found in equilibrium with their dimeric form *cis*-[$PtR_2(SR'_2)_2$] = [$Pt_2R_4(\mu$-$SR'_2)_2$] + $2R'_2S$ while organo-bis-sulfoxides were stable as monomeric *cis*-[$PtR_2(Me_2SO)_2$] species. Both series of complexes have become standard precursors to other organoplatinum compounds since the above sulfur ligands are easily displaced by other ligands L to give *cis*-[$PtR_2L_2$] species.

Starting from both *cis*-[$Pt(Me_2SO)_2R_2$] and *cis*-[$Pt(Me_2S)Ph_2$], we have already prepared platinum(II) derivatives with neutral binucleating ligands having extensively conjugated π* orbitals of low energy; they allowed a stepwise synthesis of bimetallic complexes in which metal centres exert a mutual influence mediated by the bridging ligand [5]. Furthermore, it has been shown that the transmission of electronic effects between the two metals in [$Me_2Pt(BL)PtMe_2$] complexes depends on the size, steric conformation and degree of unsaturation of the connecting binucleating ligand BL [6].

In our quest for suitable binucleating ligands, we have been attracted by N,N′di- and tetra-substituted dithioxamides. These are polyfunctional ligands possessing low-lying π* orbitals and are capable of forming polymetallic systems [7]. A number of papers has appeared on the coordination chemistry of such ligands [8], but, as far as organometallic derivatives are con-

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cerned, only a few contributions deal with tetraalkyldithioxamides of zerovalent carbonyl complexes of molybdenum [9] and rhenium [10]. To our knowledge, no papers have appeared to date concerning N,N′-disubstituted dithioxamides linked to metal fragments having a metal–carbon $\sigma$ bond.

We now report the reactions of some N,N′-dialkyl-substituted dithioxamides with *cis*-$[Pt_2L_2R_2]$ species (L = $Me_2SO$ or $Me_2S$; R = Me or Ph) and *trans*-$[Pt(Me_2SO)_2MeCl]$. The obtained products are the first reported organometallic derivatives of metal complexes containing N,N′-disubstituted dithioxamide.

## 2. Experimental

*cis*-$[Me_2Pt(Me_2SO)_2]$ [4], *cis*-$[Ph_2Pt(Me_2SO)_2]$ [11], *cis*-$[Ph_2Pt(Me_2S)_2]$ [12] and *trans*-$[Pt(Me_2SO)_2MeCl]$ [4] were prepared according to literature procedures. $H_2$-$Me_2$-DTO, $H_2$-$bz_2$-DTO and $H_2$-$bu_2$-DTO were synthesised following the method of Hurd et al. [13].

Other reagents were commercially available and used as purchased. Solvents were freshly distilled over sodium wire under a nitrogen atmosphere.

IR spectra were obtained as nujol mulls on a Perkin-Elmer FT IR 1720 X model spectrometer. $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 300.13 and 125.497 MHz, respectively, on a Bruker AMX-R 300 spectrometer. Proton chemical shifts were referenced to the residual solvent peak and reported versus TMS. $^{31}P$ chemical shifts were reported versus aqueous $H_3PO_4$ (85%) as external standard. Variable temperature experiments were performed using a Bruker VT controller and the temperature was checked by a home-built thermocouple.

### 2.1. *Preparation of complexes*

#### 2.1.1. *[PtLR(H-R′₂-DTO)] (L = Me₂SO and Me₂S; R = Me and Ph; R′ = methyl, benzyl and n-butyl)*

A weighed amount of the desired *cis*-$[L_2PtR_2]$ substrate (L = $Me_2SO$ or $Me_2S$; R = $-C_6H_5$ or $-CH_3$) was dissolved in $C_6H_6$ and reacted with the stoichiometric quantity of $H_2$-$R'_2$-DTO. The solution became red–orange, and was allowed to stand for 30 min. Upon concentration, red crystals of [PtL(X)(H-$R'_2$-DTO)] separated out.

Yield was determined only for [Pt($Me_2SO$)Me(H-$bz_2$-DTO)] which was prepared starting from 300 mg of *cis*-$[PtMe_2(Me_2SO)_2]$; it was almost quantitative, except for recovery loss. Other complexes were prepared in a small scale, just enough for NMR spectra and microanalyses (C, H, N). Elemental analyses were satisfactory, see Section 4.

#### 2.1.2. *[PtCO(Me)(H-bz₂-DTO)]*

50 mg of [Pt($Me_2SO$)Me(H-$bz_2$-DTO] were dissolved in 20 ml of benzene and carbon monoxide was bubbled for 4 h into the resulting solution. After concentration, 22 mg of pure [PtCO(Me)(H-$bz_2$-DTO)] were collected as magenta powder (see also Section 4).

#### 2.1.3. *[PtPPh₃(Me)(H-bz₂-DTO)]*

50 mg of [($Me_2SO$)MePt(H-$bz_2$-DTO)] were dissolved in 20 ml of benzene and then reacted with the stoichiometric amount of $PPh_3$. After concentration, 32 mg of pure [Pt$PPh_3$(Me)(H-$bz_2$-DTO)] were collected as a red-orange microcrystalline powder (see also Section 4).

#### 2.1.4. *[Pt((Me₂N)₂CS)Me(H-bz₂-DTO)]*

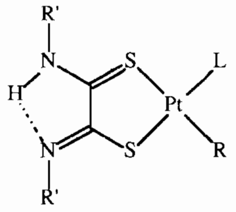
80 mg of [Pt($Me_2SO$)Me(H-$bz_2$-DTO)] were dissolved in 20 ml of benzene and then reacted with a twofold amount of tetramethylthiourea. After standing for 30 min, the solvent was removed and the residue, dissolved in the minimum amount of $CHCl_3$, was placed at the head of an alumina preparative column and then eluted with a benzene/chloroform (3:7) mixture. The coloured portion of the eluate was concentrated and 23 mg of pure [Pt(($Me_2N)_2$CS)Me(H-$bz_2$-DTO)] were collected as red powder (see also Section 4).

## 3. Results and discussion

*Cis*-$[PtL_2R_2]$ complexes (R = Me or Ph; L = $Me_2SO$ or $Me_2S$) react quantitatively with the stoichiometric amount of $R'_2$-DTO according to Eq. (1).

$$cis\text{-}[PtL_2R_2] + R'_2DTO \longrightarrow \underset{\mathbf{1}}{[PtL(R)(H_2\text{-}R'_2\text{-}DTO)]} + L + RH \qquad (1)$$

We are able to assign to the formed compounds the molecular geometry shown below on the basis of $^1H$ NMR evidences (spectral data are given in Table 1):



(i) N,N or S,N coordination can be ruled out, since, in such a case, one could expect the methylene splitting of one or both signals of the alkyl substituents on N, due to coupling with $^{195}Pt$;

(ii) alkyl chain hydrogens of R′ substituents appear in the spectrum as a pair of equally intense signals;

Table 1
Selected $^1$H NMR parameters for [PtL(R)(H-R$'_2$-DTO)] complexes (R = Me or Ph, L = $Me_2SO$ or $Me_2S$). Chemical shifts are given in ppm (TMS as reference). The value of the coupling constants $^3J$(Pt–H) and $^2J$(Pt–H) (in Hertz) are indicated in parentheses beside the corresponding $\delta$ values

| | $\delta$(N–$CH_2$–R″)<br>(R″ = H, $C_3H_7$, $C_6H_5$) | $\delta$(Pt–S–$CH_3$) | $\delta$(Pt–$CH_3$) |
|---|---|---|---|
| L = $Me_2SO$, R = Me, R′ = Me[a] | 3.51, s, 3H<br>2.47, s, 3H | 2.54 (26.5), s, 6H | 0.965 (73.2), s, 3H |
| L = $Me_2SO$, R = Me, R′ = $^n$bu[b] | 3.68, t, 3H<br>3.66, t, 3H | 3.31 (26), s, 6H | 0.51 (71.8), 3H |
| L = $Me_2SO$, R = Me, R′ = bz[a] | 5.06, s, 2H<br>4.29, s, 2H | 2.49 (26.6), s, 6H | 0.94 (73.4), 3H |
| L = $Me_2SO$, R = Ph, R′ = Me[a] | 3.44, s, 3H<br>2.45, s, 3H | 2.4 (27.2), s, 6H | |
| L = $Me_2SO$, R = Ph, R′ = $^n$bu[b] | 3.73, t, 2H<br>3.59, t, 2H | 3.05 (27.4), s, 6H | |
| L = $Me_2SO$, R = Ph, R′ = bz[a] | 4.96, s, 2H<br>4.3, s, 2H | 2.4 (27.6), s, 6H | |
| L = $Me_2S$, R = Ph, R′ = Me[a] | 3.09, s, 3H<br>2.90, s, 3H | 1.93 (50), s, 6H | |
| L = $Me_2S$, R = Ph, R′ = $^n$bu[b] | 3.69, t, 2H<br>3.61, t, 2H | 2.44 (49), s, 6H | |
| L = $Me_2S$, R = Ph, R′ = bz[a] | 4.76, s, 2H<br>4.66, s, 2H | 1.91 (49.6), s, 6H | |

[a] $C_6D_6$ solvent.
[b] $CDCl_3$ solvent.

(iii) S coordinated $Me_2SO$ and $Me_2S$ exhibit $^3J$(Pt–H) coupling constants of about 26 and 50 Hz, respectively, while in the starting materials *cis*-[$PtL_2R_2$] the above coupling constants were of about 14 ($Me_2SO$ complexes) and 25 ($Me_2S$ complexes) Hz. The increased $^3J$(Pt–H) value confirms that a $\sigma$-bonded organo group *trans* to $Me_2SO$ or $Me_2S$ has been replaced by the S=C= moiety of the chelating DTO, which exerts a remarkably lower *trans* influence.

Furthermore, the NH resonance was not detected in the spectrum over a wide spectral window, nor were the N–$CH_2$– hydrogens coupled with the N–H protons as in the free DTO ligand. This could mean that the residual amidic hydrogen in the rubeanate frame of the molecule, 'buried' between two nitrogen atoms as in proton sponges, is in a fast exchange with both amidic nitrogens.

Reaction (1) seems to be peculiar because the *cis*-[$PtL_2R_2$] complexes (L = $Me_2S$ or $Me_2SO$) behave as sources of PtLR moieties, and we know that these starting materials are considered, as stated above, standard precursors for organometallic complexes containing the $PtR_2$ fragment.

Furthermore, we have recently observed that tetraethyldithioxamide, when reacted with *cis*-[Pt($Me_2SO$)$_2R_2$], behaves like other common neutral chelating ligands and gives rise to [Pt(L-L)$R_2$] complexes [14]. Clearly, the different reaction course of *N,N′*-dialkyldithioxamides with respect to other chelating ligands is due to the two amidic hydrogens in the ligand which are capable to produce the cleavage of one of the two Pt–C bond in *cis*-[$PtL_2R_2$]. The splitting of the platinum(II)–carbon bond [2] can be produced by many processes including thermal decomposition, $\beta$-hydride elimination, reactions with molecular hydrogen or halogens, oxidative addition of alkyl halides followed by reductive elimination of alkanes, and then protonolysis.

Reaction (1) is formally a protonolysis process, unusual as it may seem. In fact, it has generally been observed that protonolysis of the Pt–C $\sigma$ bond is produced by strong mineral acids, while very weak acids such as alcohols, thiols or terminal alkynes can only hydrolyse palladium(II)–C $\sigma$ bonds [15]. We know that amidic hydrogens have an acid strength comparable to that of alcohols; hence it seems hard to understand how the hydrogen atoms of dialkyldithioxamides cleave the Pt–C bond in *cis*-[$PtR_2L_2$].

In view of the above we think that any reaction scheme can only be tentative and the assessment of the mechanism must await a detailed kinetic study of the reaction.

It is interesting to compare the behaviour of *cis*-[Pt($Me_2SO$)$_2R_2$] to that of the Werner classic compound *cis*-[Pt($Me_2SO$)$_2Cl_2$] in the reaction with N,N′-dialkyl-substituted dithioxamides. As shown previously, *cis*-[Pt($Me_2SO$)$_2$$Cl_2$] reacts with a stoichiometric amount of $^n$bu$_2$-DTO giving rise to the monochelate ion pair {Pt($Me_2SO$)Cl($H_2$-$^n$bu$_2$-DTO)$^+$,($Cl^-$)} [16]. Thus, for both organometallic substrates *cis*-[Pt($Me_2SO$)$_2$$R_2$] or the corresponding coordination compound *cis*-[Pt($Me_2SO$)$_2$$Cl_2$], it is possible to write a unique reaction representing the stoichiometry (Eq. (2)), the only

$$cis\text{-}[\mathrm{Pt(Me_2SO)_2X_2}] + \mathrm{H_2\text{-}R'_2\text{-}DTO} \longrightarrow$$
$$[\mathrm{Pt(Me_2SO)X(H\text{-}R'_2\text{-}DTO)}] + \mathrm{HX} + \mathrm{Me_2SO} \quad (2)$$

difference being that, when X = R, the hydrocarbon RH leaves the coordination spheres of platinum(II), while, when X = Cl, the hydrochloric acid HCl remains as a guest in the ion pair {Pt($Me_2So$)Cl($H_2$-$R_2$-DTO)$^+$,($Cl^-$)}.

In other words, it is evident that *cis*-[Pt($Me_2SO$)$_2$$X_2$] (X = Cl or R) species are sources of Pt($Me_2SO$)X fragments when both are reacted with $H_2$-$R_2$-DTO ligands. Hence we have considered it worthwhile to react dialkyldithioxamide ligands with the complex *trans*-[Pt($Me_2SO$)$_2$MeCl], which contains both Pt($Me_2SO$)Cl and Pt($Me_2SO$)Me fragments. This complex reacts quantitatively with the stoichiometric amount of $H_2$-bz$_2$-DTO according to reaction (3)

$$trans\text{-}[\mathrm{Pt(Me_2SO)_2MeCl}] + \mathrm{H_2\text{-}bz_2\text{-}DTO} \longrightarrow$$
$$\{\mathrm{Pt(Me_2SO)Me(H_2\text{-}bz_2\text{-}DTO)^+,(Cl^-)}\} + \mathrm{Me_2SO} \quad (3)$$
$$\mathbf{3}$$

The resulting tight ion pair **3** is a reactive species, and turns into the neutral compound [Pt($Me_2SO$)Cl(H-bz$_2$-DTO)] according to Eq. (4)

$$\{\mathrm{Pt(Me_2SO)Me(H_2\text{-}bz_2\text{-}DTO)^+,(Cl^-)}\} \longrightarrow$$
$$[\mathrm{Pt(Me_2SO)Cl(H\text{-}bz_2\text{-}DTO)}] + \mathrm{CH_4} \quad (4)$$
$$\mathbf{4}$$

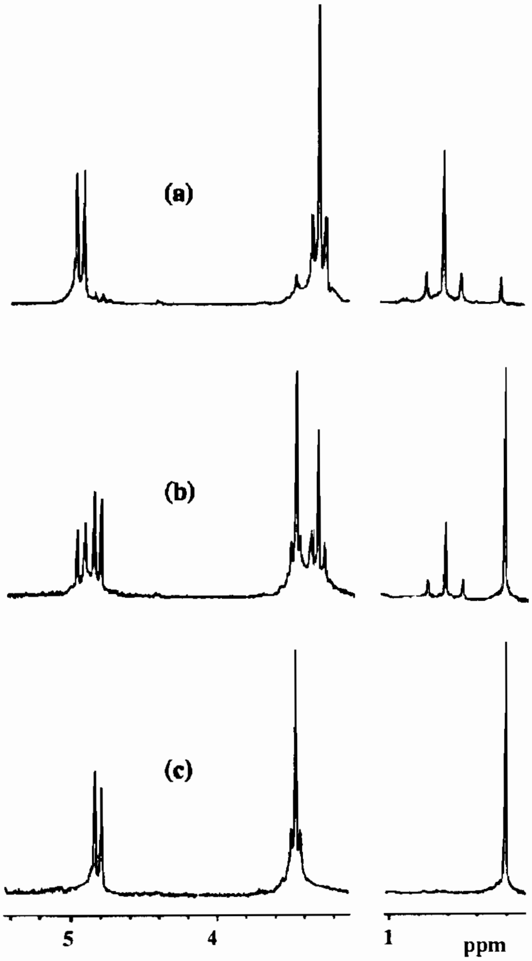


Fig. 1. $^1$H NMR spectral monitoring of the reaction *trans*-[Pt($Me_2SO$)$_2$MeCl] + $H_2$-bz$_2$-DTO. (a) Spectrum recorded immediately after the mixing of the reagents; (b) after 30 min.; (c) at the end of the reaction (see text).

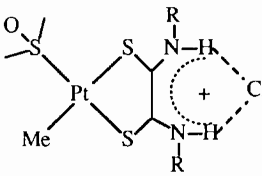
Fig. 1. shows the $^1$H NMR spectra for the above mentioned processes (spectral data are given in Table 2). The resonances of compound **3**, formed immediately after the mixing of the reagents, are clearly distinguishable (Fig. 1(a)). After 30 min, the spectrum shows the presence of a mixture of compounds **3** and **4** (Fig. 1(b)) together with methane. At the end of the reaction, only the signals attributable to complex **4** and methane are detected in solution (Fig. 1(c)). On the basis of the $^1$H NMR spectra, we assign to compound **4** a molecular formula similar to that of compounds **1** with an S,S′ chelated rubeanate frame displaying a planar C(S)–C(S) skeleton.

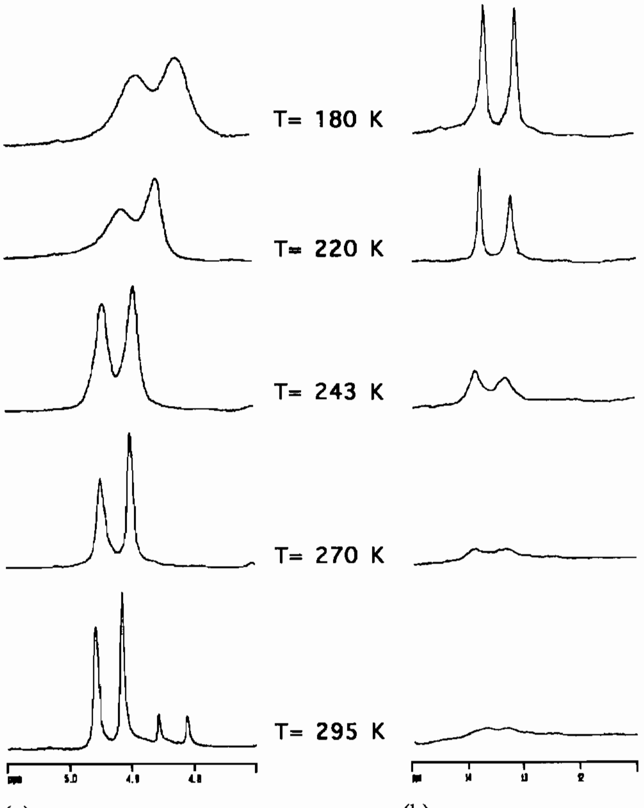
Table 2
Selected $^1$H NMR parameters for the complexes {Pt($Me_2SO$)Me($H_2$-bz$_2$-DTO)$^+$,($Cl^-$)} (**3**) and [Pt($Me_2SO$)Cl(H-bz$_2$-DTO)] (**4**). Chemical shifts are given in ppm (TMS as reference). The value of the coupling constants $^3J$(Pt–H) and $^2J$(Pt–H) (in Hertz) are indicated in parentheses beside the corresponding δ values

| | δ(N–CH$_2$–) | δ(Pt–S–CH$_3$) | δ(Pt–CH$_3$) | δ(N–H) |
|---|---|---|---|---|
| **3** | 4.96, s, 2H<br>4.90, s, 2H | 3.32 (28.7) s, 6H | 0.6 (72), s, 3H | 13.3, s<br>12.8, s |
| **4** | 4.85, s, 2H<br>4.80, s, 2H | 3.48 (19) s, 6H | | |

The same arrangement of the ligands around the platinum centre is required to describe the structure of the ion pair **3**; however in this case dithioxamide acts as a neutral ligand, and this presupposes that the two NCS moieties cannot be coplanar. In fact the coplanarity of the thioamide groups in an S,S′ coordinated neutral disubstituted dithioxamide would require a non-bonded H···H distance of ~1.4 Å between the amide protons. It should be emphasised that extremely short non-bonded H···H distances have been reported in the range 1.71–1.74 Å [17]. Thus, an S,S′ geometry in undeprotonated dithioxamides requires a torsional motion around the C–C bond between the thioamide moieties; this is a cyanine distortion since a dithioxamide is constituted by two coupled monomethyne merocyanine type units [18] and it is known that on cyanine distortion a better delocalisation of positive charge is achieved [19].

Variable temperature $^1$H NMR experiments in a $CD_2Cl_2/CDCl_3$ (90/10 vol./vol.) mixture are important to elucidate the structure of compound **3**. As shown in Fig. 2, the two singlets at 4.96 and 4.90 ppm, which are sharp and well resolved at r.t., change into broad peaks at low temperature, but unfortunately they do not decoalesce at temperatures as low as 180 K. On the nature of this dynamic process (Fig. 2(a)), we can only provide speculative comments; however, it is reasonable to assume that the rapid flipping of the thioamidic NCS moieties around the C(S)–C(S) axis becomes slower at low temperature; thus, the broadened N–$CH_2$– singlets should give rise to two sets of four AB lines at temperatures inaccessible to us. At the same time, the N–H resonances at about 13 ppm, which appear as two broad, partially superimposed peaks at room temperature, tend to coalesce as the temperature rises (Fig. 2(b)). Unfortunately, we were not able to reach a temperature high enough to see a single sharp peak for both N–H groups, because of the intrinsic reactivity of **3**. On the contrary, temperature lowering produces in the N–H region of the spectrum a fairly good separation and sharpening of the two N–H signals. This result clearly indicates that at high temperatures a rapid exchange of the amidic proton does occur; however, this process is characterised by a high activation energy, so that hydrogen atoms have a fixed arrangement in the molecule also at r.t. In addition, the values of the frequencies of the two N–H signals indicate that both N–H protons are engaged in a strong hydrogen bond of the type $^+N\text{–}H\cdots Cl^-$ [20]. This could mean that the S,S′ coordinated neutral dithioxamide in **3** acts as an anion binding agent, so that the following molecular formula could be proposed





(a) (b)

Fig. 2. Temperature dependencies on benzyl (a) and N–H (b) resonances of $\{Pt(Me_2SO)(CH_3)(H_2\text{-}bz_2\text{-}DTO)^+,(Cl^-)\}$.

The chemistry of anion binding receptors is a recent topic and little mention of these species has appeared in the literature [21]. We are well aware that the proposal of the $N\text{–}H\cdots(Cl^-)\cdots H\text{–}N$ interaction should be confirmed by a crystal structure determination, but unfortunately our attempts to grow a single crystal of **3** making use of the standard techniques were unsuccessful, because of the intrinsic reactivity of this ion.

The new complexes [PtL(R)(H-R′$_2$-DTO)] (L = $Me_2SO$ or $Me_2S$) seem to be useful starting materials for accessing to a wide class of organometallic compounds of formula [PtL′(R)(H-R′$_2$-DTO)] (L′ = neutral ligands).

From our experiments, both $Me_2SO$ and $Me_2S$ seem to be replaceable only by neutral ligands which can be classified as 'soft' bases, such as carbon monoxide, phosphines and thioureas. Table 3 summarises the $^1$H NMR spectral data for these new complexes prepared by metathesis. Obviously, the simple substitution of $Me_2SO$ or $Me_2S$ by a neutral ligand implies that the molecular geometry of the starting compounds is retained in the products. The NMR parameters in Table 3 confirm the already claimed S,S′ Pt geometry of the chelated rubeanate. The large values of the *J*(Pt–P) coupling constants in the $^{31}$P-NMR spectra indicate that phosphine ligands are opposite to low *trans* activating groups as expected if a $PR_3$ group replaces thioether or sulfoxide in **1**.

Neither Pt–P nor Pt–P–H coupling constants appear to be dependent on basicity or steric hindrance of the phosphine ligand. This is an expected result, since it is known that $^2J$(Pt–P) magnitude depends mainly on the *trans* activating power of the group opposite to phosphorus ligand; furthermore, it has been stated that

Table 3
Selected $^1$H and $^{31}$P NMR parameters for [PtL′(Me)(H-bz$_2$-DTO)] complexes (L′ = CO, PR$_3$, Me$_2$–N(=S)–NMe$_2$). Chemical shifts are given in ppm (TMS or $H_3PO_4$ as reference). The value of the coupling constants $^3J$(Pt–H), $^2J$(Pt–H) $^2J$(Pt–P–H) and $J$(Pt–P) (in Hertz) are indicated in parentheses beside the corresponding δ values

| | δ(N–CH$_2$–) | δ(Pt–CH$_3$) | δ(Pt–P) |
|---|---|---|---|
| P(Ph)$_3$[b] | 4.9, s, 2H<br>4.58, s, 2H | 0.527 (71.6[d], 5.3[e]) s, 3H | 23.88 (3746) |
| P(*m*-tolyl)$_3$[a,b] | 4.91, s, 2H<br>4.61, s, 2H | 0.534 (72.2[d], 5.08[e]), s, 3H | 23.74 (3743) |
| P($^n$bu)$_3$[a,b] | 4.87, s, 2H<br>4.81, s, 2H | 0.534, (72.7[d], 5.08[e]), s, 3H | 3.81 (3549) |
| P(Cy)$_3$[a,b] | 4.85, s, 2H<br>4.80, s, 2H | 0.564 (73[d], 3.75[e]), s, 3H | 24.25 (3566) |
| P(CH$_2$–CH$_2$–CN)$_3$[a,b] | 4.89, s, 2H<br>4.82, s, 2H | 0.473 (68.5[d], 5.75[e]), s, 3H | 14.91 (3652) |
| Tetramethylthiourea[b] | 4.81, s, 2H<br>4.75, s, 2H<br>3.2, s, 12H[f] | 0.55 (73.6), s, 3H | |
| CO[c] | 4.93, s, 2H<br>4.25, s, 2H | 1.41 (73.42), s, 3H | |

[a] Complexes characterized only in solution.
[b] $CDCl_3$ as solvent.
[c] $C_6D_6$ as solvent; for the carbonylic complex ν(CO) stretching frequency is 2061 cm$^{-1}$ (nujol mull).
[d] $^2J$(Pt–H).
[e] $^4J$(Pt–P–H).
[f] Methyl singlet of coordinated tetramethylthiourea.

the values of $J$(Pt–P–H) are not correlated to any structural property in methylplatinum phosphine complexes [22]. Finally, it should be noted that neutral ligands classified as 'hard' bases such as alkylamines, anilines and pyridines do not substitute Me$_2$SO and Me$_2$S in [PtL(R)(H-R′$_2$-DTO)] even if reacted in a large ligand to metal ratio. In addition, it is useful to remember that dithioamidic ligands do not give rise to any observable reaction when they are reacted even in great excess with respect to [PtL(R)(H-R$_2$-DTO)].

We have not yet a definite explanation for the observed selective reactivity of [PtL(R)(H-R′$_2$-DTO)]. However, it is possible that these new organoplatinum complexes offer the opportunity of studying steric and electronic ligand effects because of the possibility of varying selectively the ligand L.

## 4. Supplementary material

Further details on elemental analysis (Table S1) are available from the authors on request.

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